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(54) Title: SELF-SUSTAINING HYDROGEN GENERATOR			
(57) Abstract			
<p>A self-starting, self-sustaining hydrogen generator comprises a reactor packed with a mass of mixed catalyst, containing supported copper and palladium. A feedstock, of e.g. methanol and an oxygen source such as air, is injected at high velocity into the mass of catalyst through multipoint entry such as a tube of porous ceramic. The mass of catalyst is preferably configured concentrically around the tube injector, so that the fluid-flow follows a radial path through the reactor. The product gas is high in hydrogen and can be used as a feed for a fuel cell.</p>			

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Self-sustaining hydrogene generator

This invention concerns improvements in reformers, more especially
it concerns improvements in self-sustaining reformers that start-up from ambient
temperature. The volume-specific hydrogen output of these improved reformers
5 makes them suitable for application in fuel-cell powered vehicles.

We have disclosed in EP 0 217 532, a self-igniting partial oxidation
reformer or catalytic hydrogen generator which has become known as the "Hot Spot"
10 reactor. The basic concept is that methanol and air are co-fed into a reactor
containing a packed bed of copper on refractory support catalyst, with a down-stream
zone containing platinum or palladium catalyst mixed with copper catalyst. The
down-stream zone provides self-ignition to raise the reactor temperature to a point

at which a hot spot formed around the point of injection of feedstock into the bed of catalyst. This concept was further developed in the invention of EP 0 262 947, which uses this reactor design to produce hydrogen from hydrocarbons, but using a catalyst composed of platinum and chromium oxide on a support. Further details have been given in a paper in Platinum Metals Review, 1989, 33, (3) 118-127.

5

As predicted in the above-mentioned prior art, the use of liquid fuels as hydrogen sources for fuel-cell powered vehicles, or even static systems, is attracting considerable interest. The best established conversion system is steam reforming, but this is an endothermic reaction, requiring continuous input of energy. Whilst self-sustaining reforming is clearly an interesting concept, in further studies of the Hot-Spot system, we have found that the reactor as described did not permit scale-up, and therefore there was a need to find alternative and improved reactor and/or system designs.

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The present invention provides a self-igniting and self-sustaining hydrogen generation reactor for a feedstock comprising an organic fuel in liquid, atomised (spray), vapour or gas form and a source of oxygen, such as air, said reactor comprising a permeable fixed bed of copper-supported catalyst and a PGM-supported catalyst, said reactor further comprising an inlet for the feedstock which comprises a multipoint entry causing high velocity feedstock injection into the bed together with a significant pressure drop and gas expansion, for example an extended surface area of porous ceramic. Preferably, the inlet is in the form of a porous

ceramic tube having a closed end, but other inlet designs may give advantages in particular circumstances.

The invention also provides a method for the production of hydrogen from a feedstock comprising an organic fuel and a source of oxygen, such as air, and over a mass of catalyst comprising copper and palladium or other PGM moieties, characterised in that the fuel is in spray, vapour or gas form and further characterised in that the feedstock enters a radial catalyst bed at a multipoint entry which causes a significant pressure drop and results in high velocity injection of feedstock into the bed. For example the multipoint entry may be by means of an inlet having an extended surface area of porous ceramic.

The porous ceramic used in initial tests was a commercial ceramic of pore size 100µm, purchased from Fairey, England, and this material is therefore recommended, but we expect that alternative porous ceramic materials will provide substantially similar results. It appears that porous metal inlets, whilst having similar gas flow characteristics to porous ceramics, are unsuitable because heat conduction interferes with the reactions being carried out, and could even cause premature ignition of the methanol/air mixture, for example within the feed tube. However, it is possible that further material developments, and/or further reactor design improvements, may permit composite metal/ceramic inlet design, which may bring advantages, such as in structural strength.

The organic fuel can be a hydrocarbon or an oxygenate, either in the liquid or gas phase. For ease of description, a liquid oxygenate, methanol, will be referred to in the following description.

5 In the method of the invention, a hot zone forms around the region where the feedstock enters the mass of catalyst. It is believed that this hot zone is preferably at a temperature of 350-600°C. In this zone, methanol is partially oxidised to form CO₂ and H₂, and some CO. In a preferred embodiment, water is co-fed with the methanol. The presence of water has several beneficial effects:

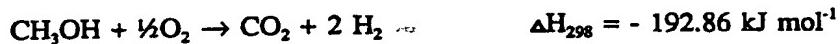
- 10 (i) It promotes the water-gas shift reaction; thus improving the efficiency of the generator and lowering the concentration of CO in the reformat from 2-8% to 1-5% by volume, and raising concurrently the H₂ concentration.
- (ii) It allows greater thermal control within the catalyst bed.
- (iii) Under some conditions, it can react directly with methanol by steam reforming, leading to a high yield of H₂.

15 The water can be pre-mixed with the methanol feed. The water concentration in the aqueous mixture should be between 1% and 40% by mass, with the preferred concentration being in the range 10-30%.

20 Conventional hydrogen-generators that depend solely or predominantly on the steam-reforming of an organic reactant require continuous input of energy during operation to supply the endothermic heat of reaction. For example, where the organic reactant is methanol:



In the present invention, self-sustaining hydrogen generation is achieved by catalysing the exothermic conversion of the reactant, so obviating the need for continuous input of energy:



We have discovered that Cu-based catalysts are very effective for the latter reaction. It is necessary, however, to add a small amount of precious metal 10 catalyst to provide auto-ignition, and to raise the catalyst bed temperature to a level at which the partial oxidation becomes self-sustaining. When the precious metal catalyst is Pd/SiO₂, containing 3% palladium by mass, it needs only to be present as 5% of the total mass of the catalyst bed in order to induce ignition from room temperature. Other pre-heating methods may be used, however.

15

It is believed, although we do not wish to be limited to any expression of theory, that there are several key physical and chemical features in the design of an effective self-sustaining partial-oxidation reformer. The flow restriction caused by the porous ceramic creates a pressure drop, resulting in the pore openings acting as small injection points that supply fluid flow at high velocity into the catalyst bed. Then, in order for the conversion of methanol to occur exclusively by the catalytic 20 partial-oxidation route, both the following conditions must apply within the catalyst bed:

- (a) the reactant velocity must exceed the homogeneous flame speed,

- (b) the catalyst must be active enough for the heterogeneous reaction to occur within the short residence time.

To eliminate the possibility of product hydrogen undergoing oxidation, 5 it must be prevented from re-entering a high temperature region in which oxygen is present. To do this, the pressure drop across the ceramic must be high enough to prevent back-flow of products. If the porous ceramic is in the form of a tube or cylinder, the catalyst bed should be arranged concentrically to allow radial flow, and so ensure a minimum path-length through the bed.

10

It is desirable to reduce or minimise the amount of CO in the product gas fed to the fuel cell. This can be achieved by one or both of passing the product gas over a selective oxidation catalyst that selectively oxidises CO in preference to hydrogen, and passing the product gas over a low temperature water-gas shift 15 catalyst.

The invention will now be illustrated by the following Examples, and with reference to the accompanying drawings which are schematic cross-sections of reactors according to the invention.

20

EXAMPLE 1

A batch of catalyst was made by adding copper(II) ethanoate (71g) to aqueous ammonia, which had been prepared by adding distilled water (3150cm³) to

a concentrated solution (0.880) of ammonia (350cm³). This ammoniacal copper-solution was added to silica spheres (Shell S980B; 750g) in a rotating blender, which was operated for 1 hour to ensure thorough mixing. The silica spheres were then isolated and washed three times with distilled water, before being dried (110°C; 5 16hr) and calcined (450°C; 2hr). Elemental analysis showed that the resultant copper-loading on the silica spheres was 1.9% (by mass). Before being loaded into hydrogen-generator, the catalyst was activated by reduction (400°C; 2hr; 10%H₂/N₂).

A schematic diagram of the hydrogen-generator is shown in Figure 1.
10 The reactor shell consisted of a stainless cylinder (height 17cm, diameter 9cm), 1, having a main inlet aperture, 2, and an outlet aperture, 3, to which was attached an outlet tube, 4. Fitted through the aperture 2 was a feedstock inlet tube, 5, having a flange, 6. Fitted and sealed to a stainless flange 6 was a porous ceramic tube, 7, held under compression by and sealed to a stainless steel clamping bar, 8. The
15 feedstock inlet tube 5 had an L-shaped manifold, 9, into which was fed an air line, 10, and a feed line for the liquid feed, 11. The liquid-feed line 11 was coiled around the inlet tube 5 for heat exchange, before terminating mid-way down the porous ceramic tube 7. In this embodiment, a further air line, 12, entered the reactor 1 and was coiled around the reactor wall, for preheating the air, before entering the
20 manifold 9. In this configuration, the fluid emerged radially from the porous ceramic tube, but it then followed an axial path through most of the catalyst bed. The volume of the catalyst bed was 850cm³.

A mixture comprising 85% methanol (by mass) in water was injected (at a rate of $5.2\text{cm}^3 \text{ min}^{-1}$) into the catalyst bed through the porous ceramic tube (dimensions: 3cm diameter, 4cm long; pore diameter: $100\mu\text{m}$). The exit stream was cooled to remove any condensable components, and the dry gas was analysed for H_2 ,
5 CO , CO_2 , O_2 and N_2 .

The bed temperature was raised (by applying an external heat source) until the onset of reaction, which occurred at *ca* 150°C ; the external heating was then switched off. The composition of the exit stream was recorded as a function of
10 time elapsed after the onset of reaction (Table 1).

A steady state was reached after about 20 minutes of operation, when the hydrogen yield levelled at $245 \text{ litres h}^{-1}$. When the volume of catalyst was taken into account, the specific output of hydrogen at steady-state was 290 litres per hour
15 per litre of catalyst. At this stage, the maximum temperature within the catalyst bed (in the immediate vicinity of the ceramic tube) stabilised at *ca* 600°C , whereas the temperature inside the tube remained $<100^\circ\text{C}$. Furthermore, the efficiency of the generator was close to 100% (*ie* each molecule of methanol converted produced 2 molecules of hydrogen). When the water was excluded from the reactant-feed,
20 the efficiency declined to 92%.

TABLE 1

Output of axial hydrogen-generator with 4cm long ceramic injector
and 850cm³ catalyst bed; composition of reformat and hydrogen-yield

5

Time elapsed

	2 min	15 min	25 min	30 min
H ₂ / %	30	31	39	39
CO / %	3	2	2	1.8
CO ₂ / %	>20	>20	18	19
O ₂ / %	0	0	0	0
N ₂ / %	37	37	39	39
H ₂ -yield / litres h ⁻¹	180	195	245	246

10

15

EXAMPLE 2

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The procedure described in Example 1 was followed, except that a longer ceramic injector (dimensions: 3cm diameter, 6cm long) was used and the reactant feed-rates were increased (85% methanol/water 7.6cm³ min⁻¹; air 9000cm³ min⁻¹). After onset of reaction, the generator reached a steady-state after about 15 minutes of operation (Table 2). In this case, the specific hydrogen output at steady state was 420 litres per hour per litre of catalyst.

25

TABLE 2

Output of axial hydrogen-generator with 6cm long ceramic injector
and 850cm³ catalyst bed; composition of reformate and hydrogen-yield.

5

Time elapsed

10

	10 min	15 min	25 min	30 min	40 min
H ₂ / %	32	35	36	36	36
CO / %	4	4	4	4.5	5
CO ₂ / %	16	16	16	16	16
O ₂ / %	0	0	0	0	0
N ₂ / %	36	36	37	37	37
H ₂ -yield / litres h ⁻¹	307	358	355	351	362

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EXAMPLE 3

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The hydrogen-generator shown in Figure 1 was modified, as shown in Figure 2, to allow radial flow through a smaller bed (120cm³) of catalyst. As Figure 2 shows, the catalyst bed, 21, was the same length (6cm) as the porous ceramic tube, 22. The bed was enclosed by a copper gauze, 23, which allowed the products to emerge radially. Axial flow through the bed was prevented by the presence of two impervious ceramic plugs, 24 and 25.

25

The catalyst was prepared and activated in the way described in Example 1. Neat methanol was injected (at a rate of 3.6cm³ min⁻¹) together with air (2500cm³ min⁻¹) into the catalyst bed through the porous ceramic tube. An external

heat source was applied, but only until the onset of reaction. After onset, a steady state was quickly reached (within 3 minutes), where the specific hydrogen output was 690 litres per hour per litre of catalyst (Table 3). By increasing the air feed-rate (to $4000\text{cm}^3 \text{min}^{-1}$), the hydrogen yield was increased to a maximum of 93 litres h^{-1} , which corresponded to a specific output of 775 litres per hour per litre of reactor.

5

TABLE 3

Output of radial hydrogen-generator with 6cm long ceramic injector and 120cm^3 catalyst bed; composition of reformat and hydrogen-yield.

10

Time elapsed

	3 min	25 min	45 min	60 min
H ₂ / %	32.5	32	33	32
CO / %	5	5.5	4	3.5
CO ₂ / %	16	15.5	16.5	16.5
O ₂ / %	0	0	0	0
N ₂ / %	43	43	42	42
H ₂ -yield / litres h^{-1}	86	80	84	81

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EXAMPLE 4

A 5%Cu/Al₂O₃ catalyst (nominal composition by mass) was prepared by adding copper(II) ethanoate (82.4g) to a concentrated solution (0.880) of ammonia (320cm³). The resultant solution was added slowly to alumina extrudate (Norton

20